

General Disclaimer

One or more of the Following Statements may affect this Document

- This document has been reproduced from the best copy furnished by the organizational source. It is being released in the interest of making available as much information as possible.
- This document may contain data, which exceeds the sheet parameters. It was furnished in this condition by the organizational source and is the best copy available.
- This document may contain tone-on-tone or color graphs, charts and/or pictures, which have been reproduced in black and white.
- This document is paginated as submitted by the original source.
- Portions of this document are not fully legible due to the historical nature of some of the material. However, it is the best reproduction available from the original submission.

X-644-70-266

PREPRINT

NASA TM X-63988

Mg^{2+} - Fe^{2+} ORDER-DISORDER AND
THE THERMODYNAMICS OF THE
ORTHO PYROXENE, $(Mg,Fe)SiO_3$,
CRYSTALLINE SOLUTION

SURENDRA K. SAXENA
SUBRATA GHOSE

JULY 1970



GSFC

— GODDARD SPACE FLIGHT CENTER
GREENBELT, MARYLAND —

N70-34345

FACILITY FORM 602

(ACCESSION NUMBER)

28

(THRU)

TMX-63988

(CODE)

06

(NASA CR OR TMX OR AD NUMBER)

(CATEGORY)

X-644-70-266

PREPRINT

**Mg²⁺-Fe²⁺ ORDER-DISORDER AND THE THERMODYNAMICS
OF THE ORTHOPYROXENE, (Mg,Fe)SiO₃ CRYSTALLINE SOLUTION**

Surendra K. Saxena

Subrata Ghose

Planetology Branch

July 1970

GODDARD SPACE FLIGHT CENTER

Greenbelt, Maryland

PRECEDING PAGE BLANK NOT FILMED.

Mg²⁺-Fe²⁺ ORDER-DISORDER AND THE THERMODYNAMICS
OF THE ORTHOPYROXENE, (Mg,Fe)SiO₃ CRYSTALLINE SOLUTION

Surendra K. Saxena

Subrata Ghose

Planetology Branch

ABSTRACT

Activity-composition relation obtained from the intra-crystalline Mg²⁺-Fe²⁺ distribution data for orthopyroxene, (Mg,Fe)SiO₃ at 500, 600, 700 and 800°C are presented. The activity coefficients are expressed as a polynomial in the mole fraction X_{Fe} according to Redlich and Kister Equations. The excess free energy of mixing is similarly expressed using Guggenheim's Equation:

$$G^E = X_{Fe} X_{Mg} \left\{ A_0 + A_1 (X_{Fe} - X_{Mg}) + A_2 (X_{Fe} - X_{Mg})^2 \right\}$$

The two constants A_1 and A_2 decrease systematically with increasing temperature. A_0 increases from 800 to 600°C but decreases again at 500°C. The orthopyroxene solution is asymmetric and the asymmetry increases with decreasing temperature. Theoretically orthopyroxene on the Fe-rich side would begin to unmix into two coexisting pyroxenes in the vicinity of 500°C.

PRECEDING PAGE BLANK NOT FILMED.

CONTENTS

| | Page |
|---|------|
| INTRODUCTION | 1 |
| ACTIVITY-COMPOSITION RELATION | 1 |
| ANALYTICAL EXPRESSIONS FOR THE ACTIVITY-COEFFICIENTS... | 3 |
| EXCESS THERMODYNAMIC FUNCTIONS | 4 |
| GENERAL CHARACTER OF THE ORTHOPYROXENE, $(\text{Mg},\text{Fe})\text{SiO}_3$ | |
| CRYSTALLINE SOLUTION | 6 |
| The Asymmetric Solution | 6 |
| Free Energy of Mixing and Critical Temperature | 7 |
| ACKNOWLEDGMENTS | 8 |
| REFERENCES..... | 9 |

Mg²⁺-Fe²⁺ ORDER-DISORDER AND THE THERMODYNAMICS
OF THE ORTHOPYROXENE, (Mg,Fe)SiO₃ CRYSTALLINE SOLUTION

INTRODUCTION

Recently Saxena and Ghose (1970) presented the Mössbauer resonance data on the distribution of Fe²⁺ and Mg²⁺ between M1 and M2 sites in orthopyroxenes heated at 500, 600, 700 and 800°C. The distribution data fit the "simple mixture" model of Guggenheim (1967) for the individual sites. In this paper the information on the solution behavior of Fe²⁺ and Mg²⁺ on each site will be used to arrive at the thermodynamic properties of mixing of Fe²⁺ and Mg²⁺ in the orthopyroxene crystalline solution as a whole. The changes in the silicate framework as a function of temperature and composition are not included in these calculations. Therefore these thermodynamic parameters are not necessarily the same as those obtained by calorimetric experiments on the solution of ferrosilite and enstatite, but they would be comparable in magnitude.

ACTIVITY-COMPOSITION RELATION

The partial activity coefficient of the Fe component with reference to a site in the orthopyroxene (Mg,Fe)₂Si₂O₆ crystalline phase is defined as

$$\ln f_{\text{Fe}}^{\text{M1}} = \frac{W^{\text{M1}}}{RT} (1 - X_{\text{Fe}}^{\text{M1}})^2 \quad (1)$$

where f_{Fe}^{M1} is the partial activity coefficient, W_{Fe}^{M1} an adjustable energy constant and X_{Fe}^{M1} the atomic fraction $Fe^{2+}/(Fe^{2+} + Mg^{2+})$ on the M1 site. The partial activity of Fe^{2+} on the M1 site is

$$a_{Fe}^{M1} = f_{Fe}^{M1} X_{Fe}^{M1} \quad (2)$$

Similarly for the M2 site,

$$a_{Fe}^{M2} = f_{Fe}^{M2} X_{Fe}^{M2} \quad (3)$$

We need a simple model of the macroscopic system, which permits the derivation of the activity of Fe component in a crystalline orthopyroxene, $(Mg, Fe)SiO_3$ phase from the partial activities of the component on individual sites M1 and M2. On the basis of statistical thermodynamics, such a model is:

$$a_{Fe}^{OPX} = (a_{Fe}^{M1} a_{Fe}^{M2})^{1/2} \quad (4)$$

Mueller (1962) used such a relation while discussing a solution model for cummingtonite. Banno and Matsui (1967) and Thompson (1970) have also used such a relationship.

Figures 1 and 2 show the plots of partial activity of Fe^{2+} against mole fraction $Fe^{2+}/(Fe^{2+} + Mg^{2+})$ on the individual sites. Figures 3, a, b, c and d show

the activity-composition relations in orthopyroxene $(\text{Fe}, \text{Mg})\text{SiO}_3$ at various temperatures. It is assumed that the silicate framework does not change significantly and its contribution to the change in activity with temperature may be neglected. Therefore $a_{\text{Fe}}^{\text{OPX}}$ is similar to $a_{\text{FeSiO}_3}^{\text{OPX}}$ in these results. Table 1 shows the activity-composition data at different temperatures. The relations presented in these figures obey the Gibbs-Duhem equation:

$$\left(X_{\text{Fe}} \frac{\partial \ln f_{\text{Fe}}}{\partial X_{\text{Fe}}} + X_{\text{Mg}} \frac{\partial \ln f_{\text{Mg}}}{\partial X_{\text{Fe}}} \right)_{PT} = 0 \quad (5)$$

ANALYTICAL EXPRESSIONS FOR THE ACTIVITY-COEFFICIENTS

It is convenient to express the activity coefficients as a polynomial in $X_{\text{Fe}}^{\text{OPX}}$. The following Redlich and Kister equations (see King, 1969) are used for this purpose:

$$\log f_{\text{Fe}} = X_{\text{Mg}}^2 \left\{ B + C (3X_{\text{Fe}} - X_{\text{Mg}}) \right\} + D(X_{\text{Fe}} - X_{\text{Mg}}) (5X_{\text{Fe}} - X_{\text{Mg}}) \quad (6)$$

$$\log f_{\text{Mg}} = X_{\text{Fe}}^2 \left\{ B - C (3X_{\text{Fe}} - X_{\text{Mg}}) \right\} + D(X_{\text{Fe}} - X_{\text{Mg}}) (5X_{\text{Fe}} - X_{\text{Mg}}) \quad (7)$$

A least squares curve is fitted to the data on activity coefficients at each temperature using the equation:

$$\log \left(\frac{f_{Fe}}{f_{Mg}} \right) = B(X_{Fe} - X_{Mg}) + C(6 X_{Fe} X_{Mg} - 1) + D(X_{Fe} - X_{Mg}) (1 - 8 X_{Fe} X_{Mg}) \quad (8)$$

The values of B, C and D are listed in Table 2.

Figure 4 shows the plots of $\log f$ against X . The curves are based on the expressions (6) and (7) and represent the experimental data well, except for those of the 500°C.

EXCESS THERMODYNAMIC FUNCTIONS

Guggenheim (1937) expressed the excess free energy of mixing G^E for a binary system as:

$$G^E = X_A X_B \{ A_0 + A_1 (X_A - X_B) + A_2 (X_A - X_B)^2 + \dots \} \quad (9)$$

where A_0 , A_1 and A_2 are related to B, C, and D as $A_0 = 2.303 RTB$, $A_1 = 2.303 RTC$, and $A_2 = 2.303 RTD$ respectively. The values of A_0 , A_1 and A_2 are listed in Table 2.

Figure 5 shows a plot of G^E against X_{Fe} at various temperatures. Note that G^E may also be calculated from the experimental data by using the relation:

$$G^E = X_{Fe} RT \ln f_{Fe} + X_{Mg} RT \ln f_{Mg} \quad (10)$$

G^E calculated for the different samples using (10) differs somewhat depending upon the fit of the analytical expressions (6) and (7) to the data on individual isotherms as shown in Figure 7.

Excess entropy of mixing, S^E and excess enthalpy of mixing, H^E can be obtained by using the general thermodynamic formulae:

$$S^E = -RT \left(X_{Fe} \frac{\partial \ln f_{Fe}}{\partial T} + X_{Mg} \frac{\partial \ln f_{Mg}}{\partial T} \right) - R(X_{Fe} \ln f_{Fe} + X_{Mg} \ln f_{Mg}) \quad (11)$$

$$H^E = -RT^2 \left(X_{Fe} \frac{\partial \ln f_{Fe}}{\partial T} + X_{Mg} \frac{\partial \ln f_{Mg}}{\partial T} \right) \quad (12)$$

GENERAL CHARACTER OF THE ORTHOPYROXENE, $(\text{Mg}, \text{Fe})\text{SiO}_3$ CRYSTALLINE SOLUTION

The Asymmetric Solution

The activity-composition diagrams (Figures 3, a to d) and the plot of G^E against X_{Fe} in Figure 5 show that the orthopyroxene solution is asymmetric. The asymmetry increases with decreasing temperature. This relation can be examined quantitatively by studying the parameters A_0 , A_1 and A_2 as a function of temperature. The expression for G^E is:

$$G^E = X_{\text{Fe}} X_{\text{Mg}} \left\{ A_0 + A_1 (X_{\text{Fe}} - X_{\text{Mg}}) + A_2 (X_{\text{Fe}} - X_{\text{Mg}})^2 \right\} \quad (13)$$

When the odd terms in the above expression vanish, the solution becomes symmetric. If A_2 and other higher terms are also zero, we obtain the model of simple mixture or the "regular" solution with A_0 as the "interchange energy" W . The asymmetry in the crystalline solution is then directly a function of the parameter A_1 .

Figure 6 shows a plot of A_0 , A_1 and A_2 against temperature. A_0 decreases systematically with temperature in the range of 600 to 800°C. A_1 and A_2 vary regularly in the entire range of experimental temperatures. The trend of variation for A_1 indicates that the asymmetry in the solution increases very rapidly with decreasing temperature. On the other hand, with increasing temperature A_1 approaches a constant value of approximately 200 cal/mole. This means

that even when A_0 and A_2 become zero (approximately at 900°C), that is, when the solution is nearly ideal, some asymmetry would still persist. Note that in the present case, a positive value of A_1 means asymmetry of the solution on the Fe rich side.

Free Energy of Mixing and Critical Temperature

The activity-composition diagram at 500°C shows a tendency for the curve to flatten as X_{Fe} approaches 0.70. This is related to the asymmetry of the solution. It appears that if A_1 increases beyond a critical value, unmixing may occur in the solution. The critical temperature should lie between 400 and 500°C. Combining the analytical expression (9) for G^E with the formulae for free energy of mixing for ideal solutions, the total free energy of mixing G^M may be calculated from the relation:

$$G^M = G^E + RT X_{Fe} \ln X_{Fe} + RT X_{Mg} RT \ln X_{Mg} \quad (14)$$

The values of A_0 , A_1 and A_2 at 400°C obtained by extrapolation are 680, 1500 and 980 cal/mole respectively. The values of G^M at various temperatures are plotted in Figure 7. The curves tend to straighten out in the Fe rich region, especially at lower temperatures. The curve at 400°C shows a compositional range ($X_{Fe} = 0.75$ to 0.90) where the orthopyroxene would unmix into two co-existing solutions one somewhat richer in Fe than the other. The critical temperature when unmixing begins may be close to 500°C.

ACKNOWLEDGMENTS

Thanks are due to Dr. R. F. Mueller for useful discussions.

REFERENCES

Banno, S., and Y. Matsui (1967) Thermodynamic properties of intracrystalline exchange solid solution. Proc. Japan Acad., 43, 762-767.

Guggenheim, E. A. (1937) Theoretical basis of Raoult's law. Trans. Faraday Soc., 33, 151-159.

Guggenheim, E. A. (1967) Thermodynamics, 5th ed. North Holland Publ. Co. Amsterdam.

King, M. B. (1969) Phase equilibrium in mixtures. Pergamon Press, London.

Mueller, R. F. (1962) Energetics of certain silicate solid solutions. Geochim Cosmochim Acta 26, 581-598.

Saxena, S. K., and S. Ghose (1970) A ⁵⁷Fe Mössbauer resonance study of the Mg²⁺-Fe²⁺ distribution in orthopyroxene (Mg, Fe)₂Si₂O₆ at 500, 600, 700 and 800°C. Amer. Mineral. (In Press).

Thompson, J. B., Jr. (1970) Chemical reactions in crystals: corrections and clarification. Amer. Mineral., 55, 528-532.

Table 1
Activity-composition Data on Orthopyroxene, $(\text{Mg}, \text{Fe})\text{SiO}_3$

| X_{Fe} | 500°C | 600°C | a_{Fe} | 700°C | 800°C |
|------------------------------|-------|-----------------|-----------------|-------|-------|
| | | | | | |
| 0.181 | 0.236 | 0.262 | | 0.245 | 0.216 |
| 0.381 | 0.499 | 0.492 | | 0.463 | 0.432 |
| 0.455 | 0.617 | 0.581 | | 0.549 | 0.509 |
| 0.500 | 0.694 | 0.625 | | - | 0.556 |
| 0.580 | 0.798 | 0.704 | | 0.668 | - |
| 0.620 | 0.825 | 0.738 | | 0.702 | 0.668 |
| 0.720 | 0.850 | 0.802 | | - | 0.755 |
| 0.760 | - | 0.823 | | - | - |
| 0.860 | - | 0.882 | | 0.877 | 0.872 |
| $X_{\text{Mg}}^{\text{OPX}}$ | | a_{Mg} | | | |
| 0.819 | 0.838 | 0.842 | | 0.837 | 0.828 |
| 0.619 | 0.638 | 0.672 | | 0.661 | 0.639 |
| 0.545 | 0.544 | 0.598 | | 0.593 | 0.569 |
| 0.500 | 0.472 | 0.545 | | - | 0.526 |
| 0.420 | 0.391 | 0.459 | | 0.473 | - |
| 0.380 | 0.378 | 0.439 | | 0.435 | 0.404 |
| 0.270 | 0.362 | 0.366 | | - | 0.321 |
| 0.240 | - | 0.340 | | - | - |
| 0.140 | - | 0.267 | | 0.223 | 0.186 |

Table 2
**Values of the Constants B, C, D, A₀, A₁ and A₂ for the Analytical
 Expressions for Log f and G^E.**

| T°C | B | C | D | cal/mole | | |
|-----|------|------|------|----------------|----------------|----------------|
| | | | | A ₀ | A ₁ | A ₂ |
| 500 | .260 | .300 | .250 | 919 | 1061 | 884 |
| 600 | .280 | .118 | .190 | 1118 | 469 | 759 |
| 700 | .212 | .060 | .130 | 944 | 267 | 579 |
| 800 | .133 | .048 | .067 | 651 | 236 | 329 |

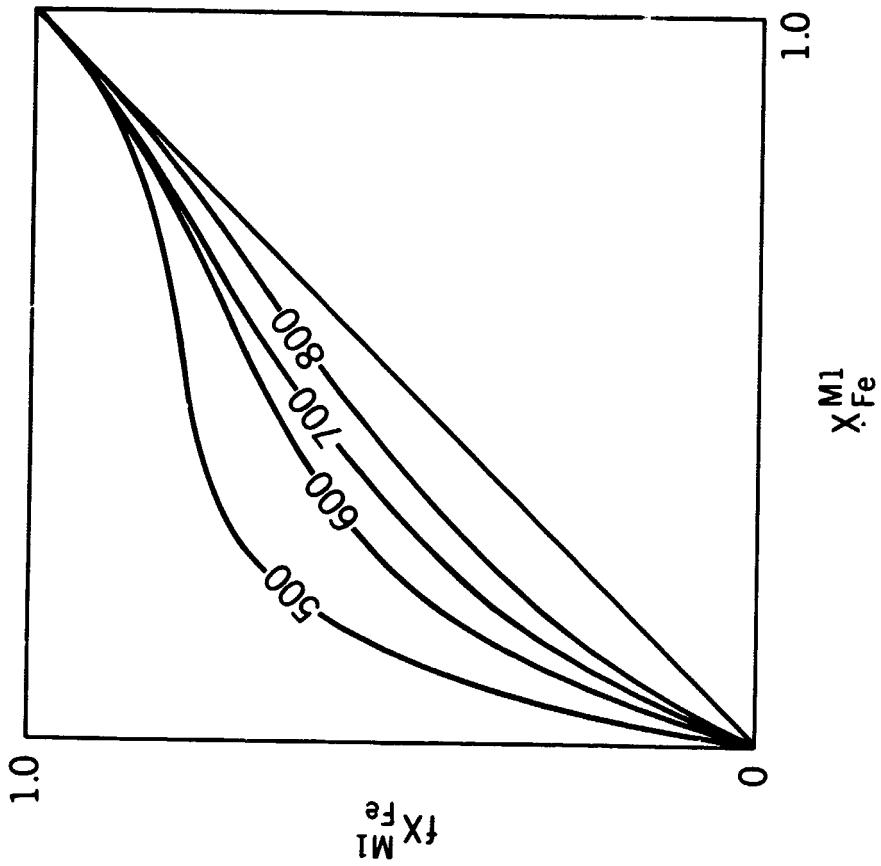


Figure 1. Partial activity-composition relation for the Mn site.

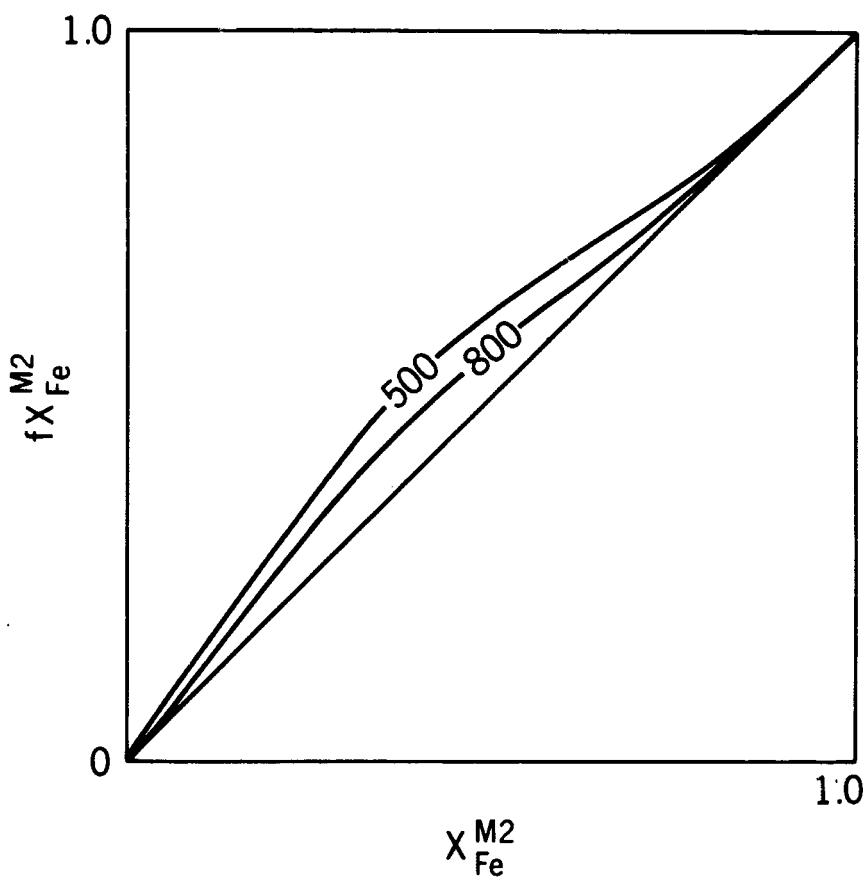


Figure 2. Partial activity-composition relation for the M2 site.

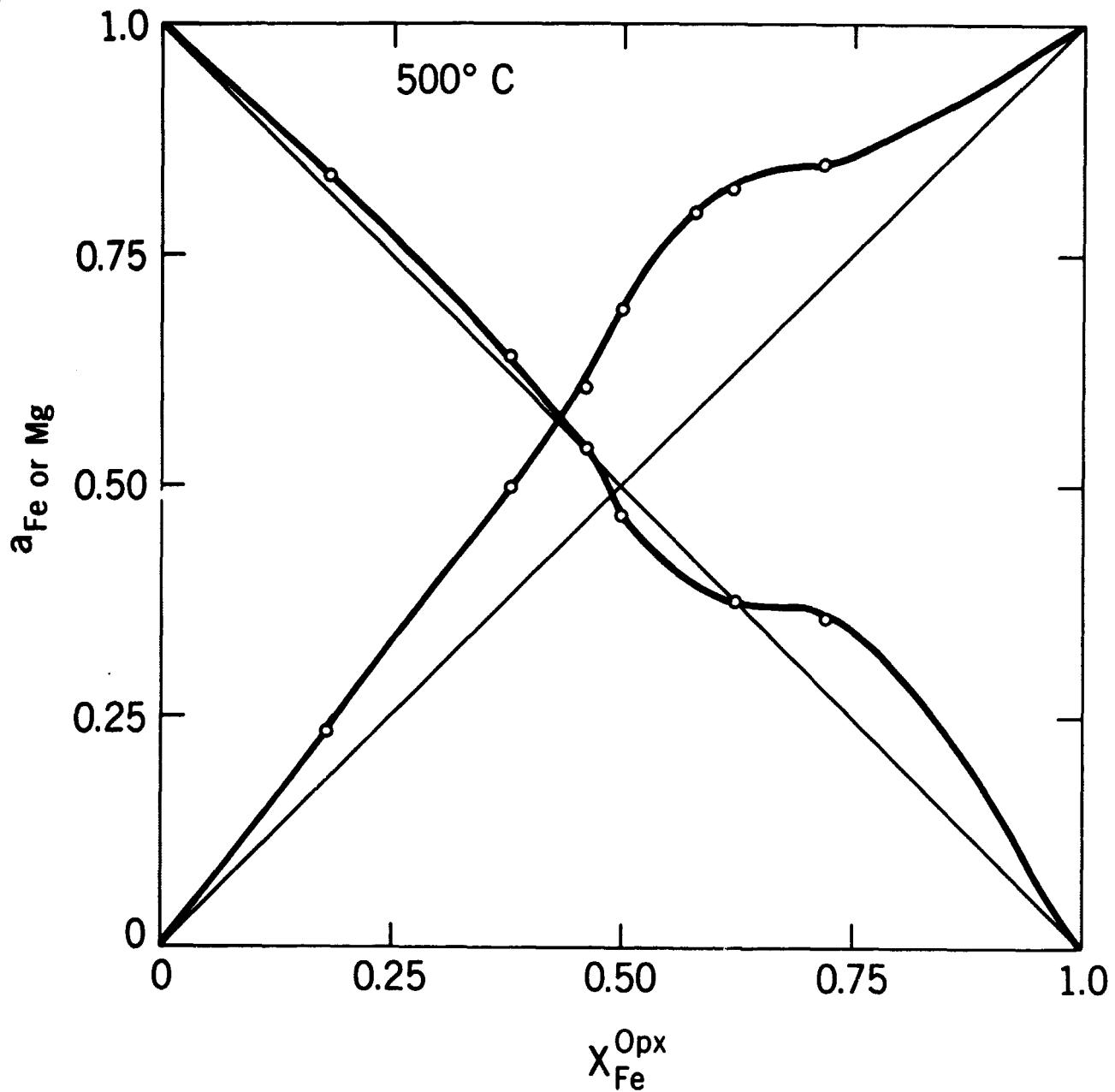


Figure 3a. Activity-composition relation in orthopyroxene, $(\text{Mg}, \text{Fe})\text{SiO}_3$ at 500°C. Smooth lines are drawn through the points.

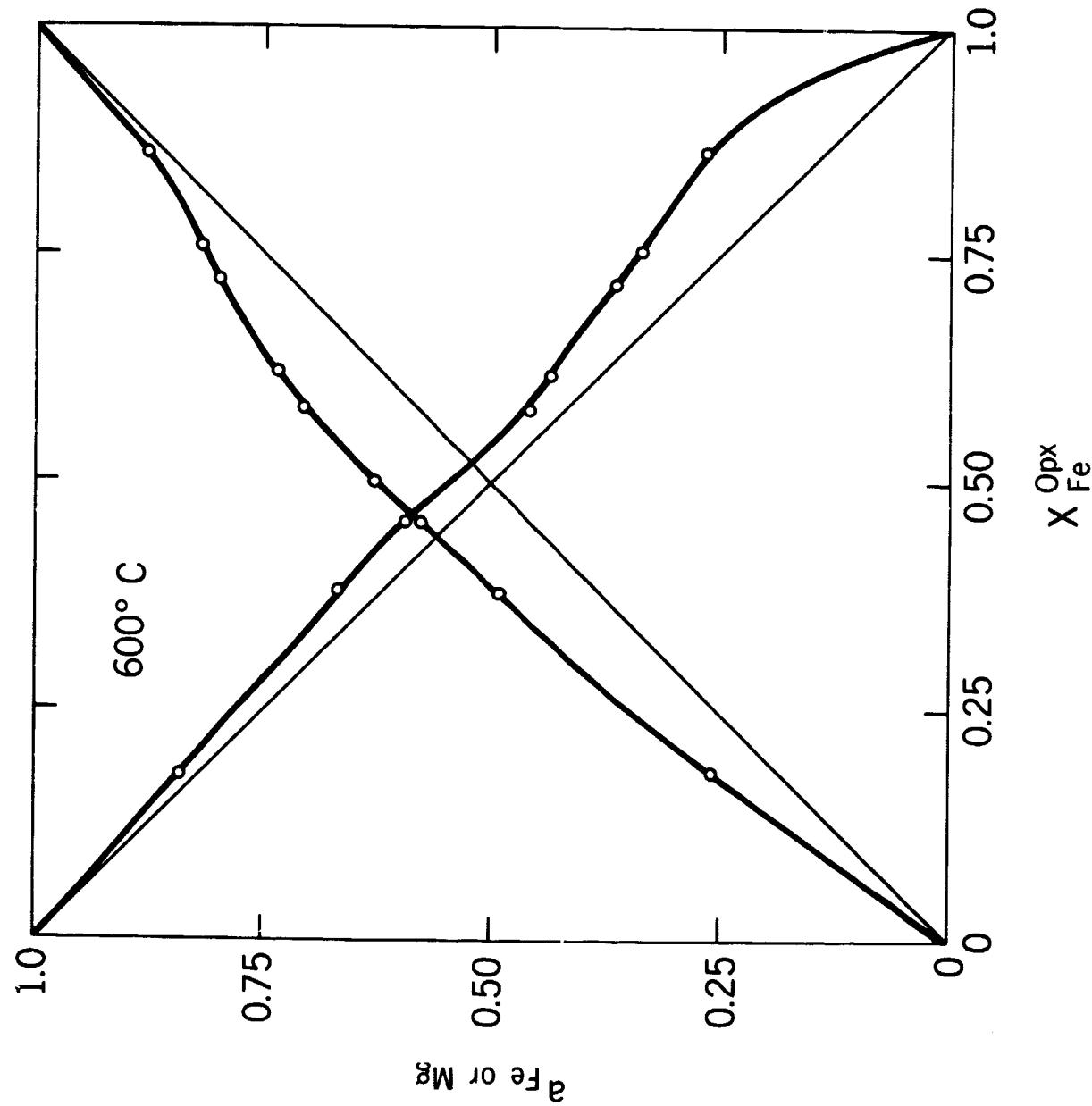


Figure 3b. Activity-composition relation in orthopyroxene, $(\text{Mg}, \text{Fe})\text{SiO}_3$ at 600°C . Smooth lines are drawn through the points.

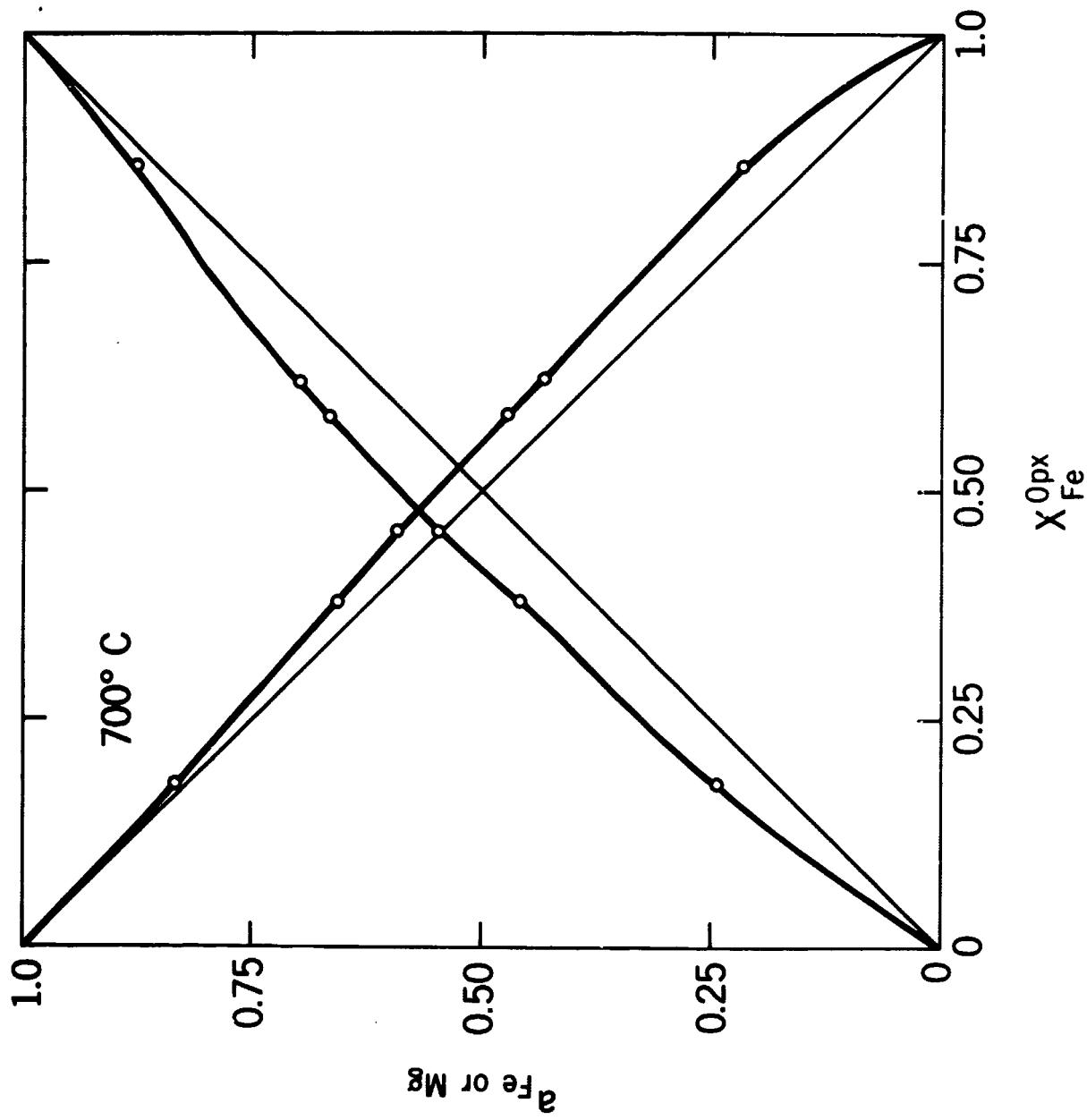


Figure 3c. Activity-composition relation in orthopyroxene, $(\text{Mg}, \text{Fe})\text{SiO}_3$ at 700°C . Smooth lines are drawn through the points.

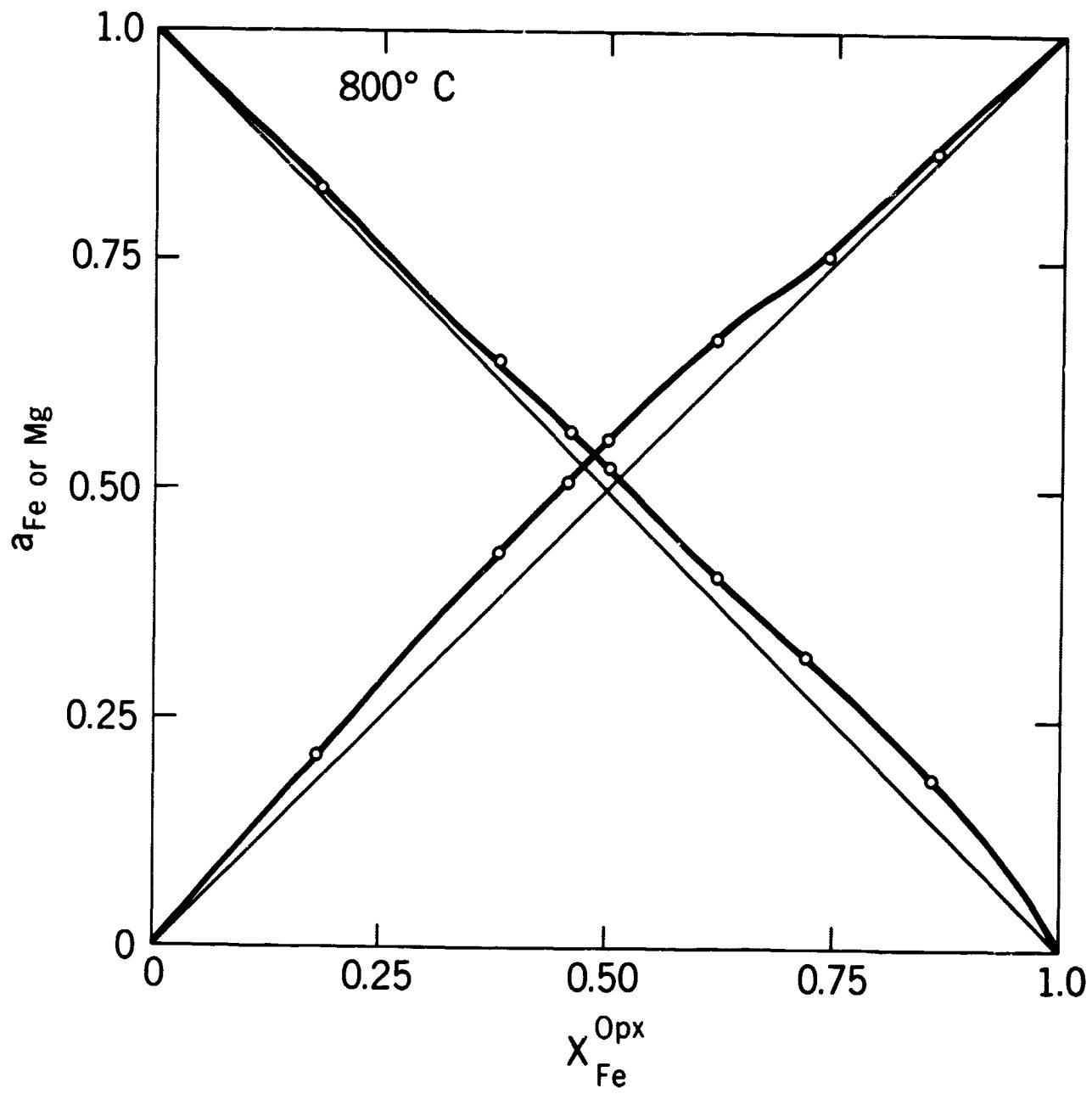


Figure 3d. Activity-composition relation in orthopyroxene, $(\text{Mg}, \text{Fe})\text{SiO}_3$ at 800°C. Smooth lines are drawn through the points.

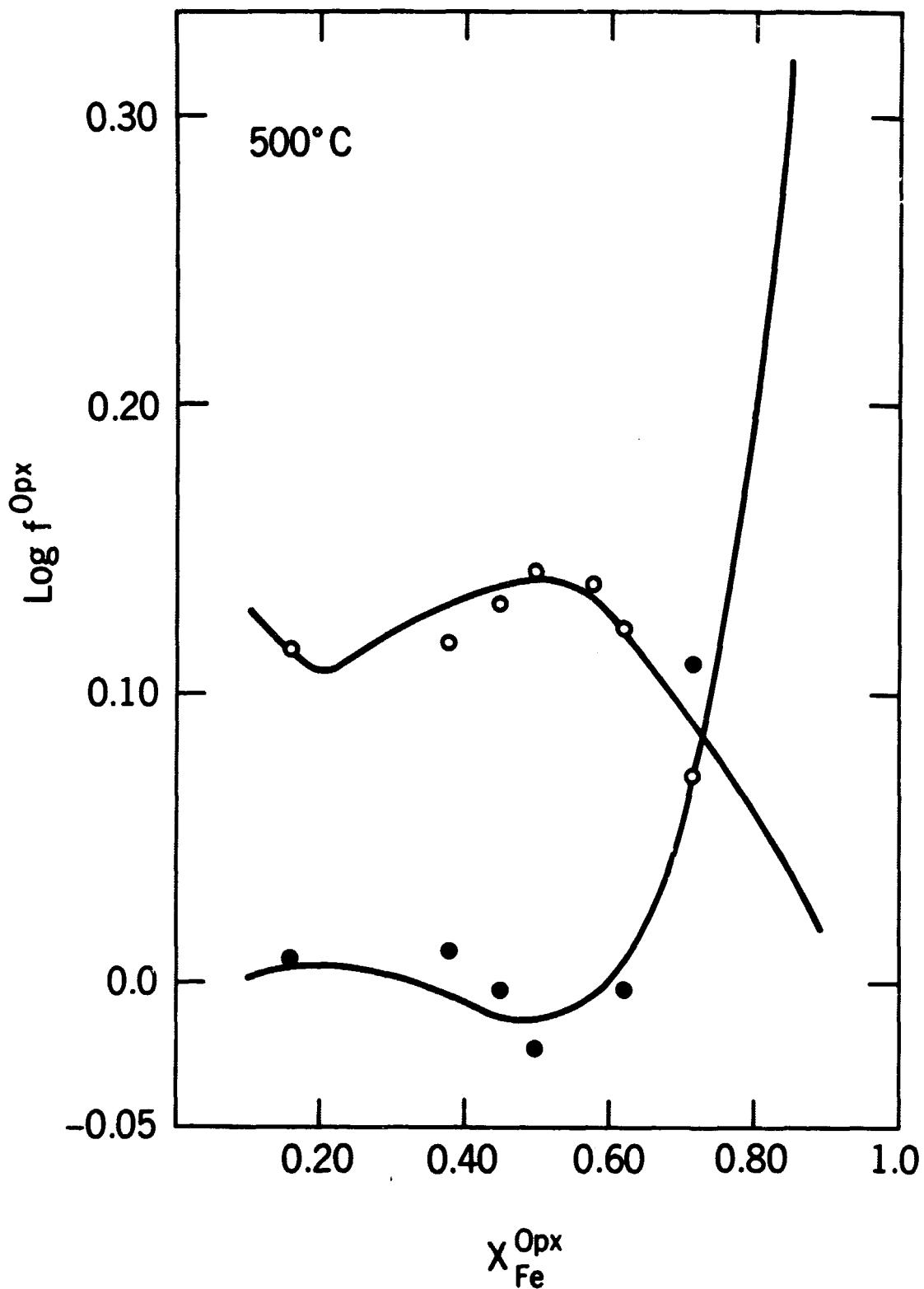


Figure 4a. Plot of $\log f$ against $X_{\text{Fe}}^{\text{Opx}}$ at 500°C . Open circles - $\log f_{\text{Mg}}$. Filled circles - $\log f_{\text{Fe}}$. The least squares curves are based on the analytical expression with three constants B, C and D due to Redlich and Kister (King, 1969).

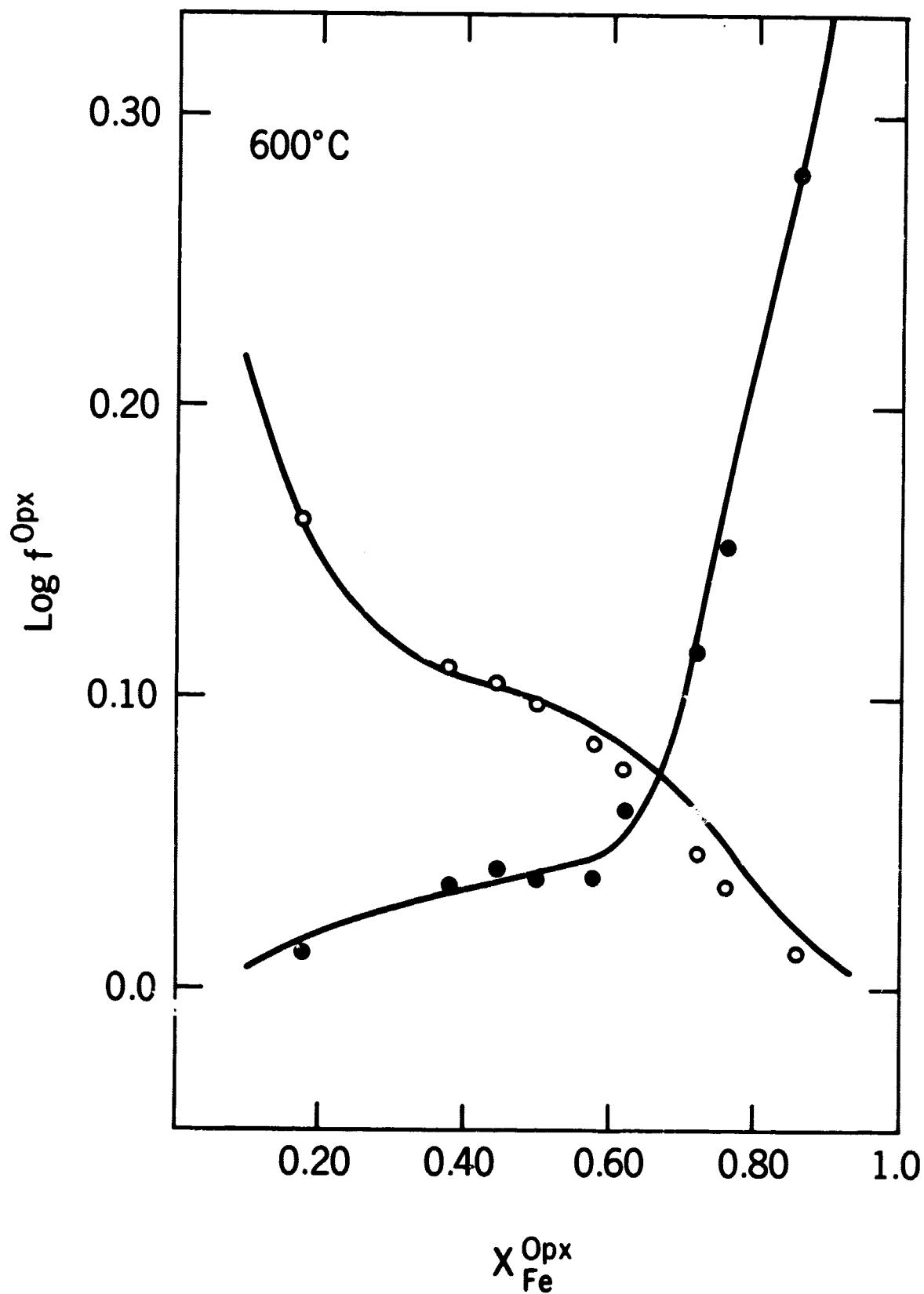


Figure 4b. Plot of log f against X_{Fe}^{Opx} at 600°C.

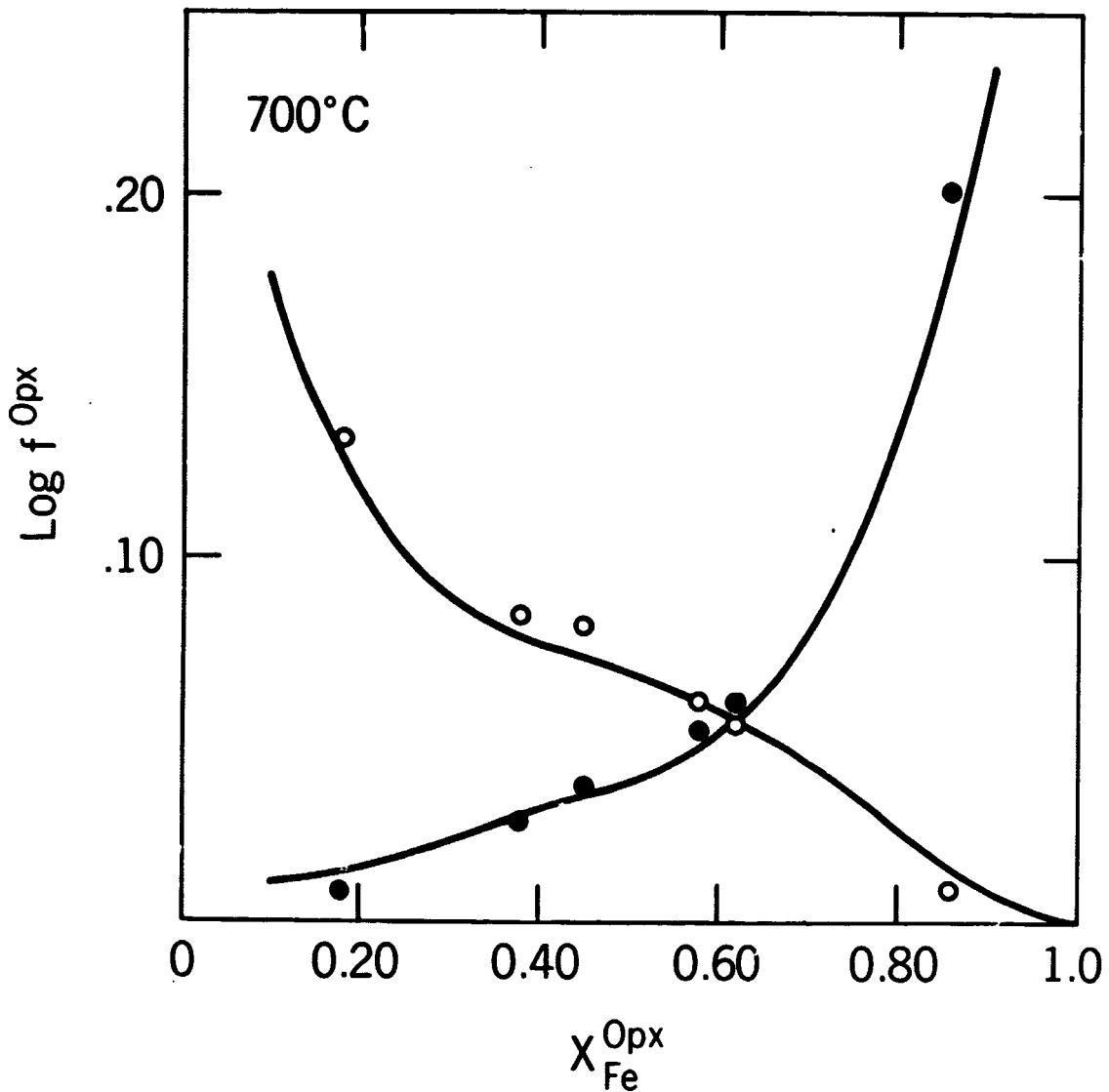


Figure 4c. Plot of log f against X_{Fe} at 700°C.

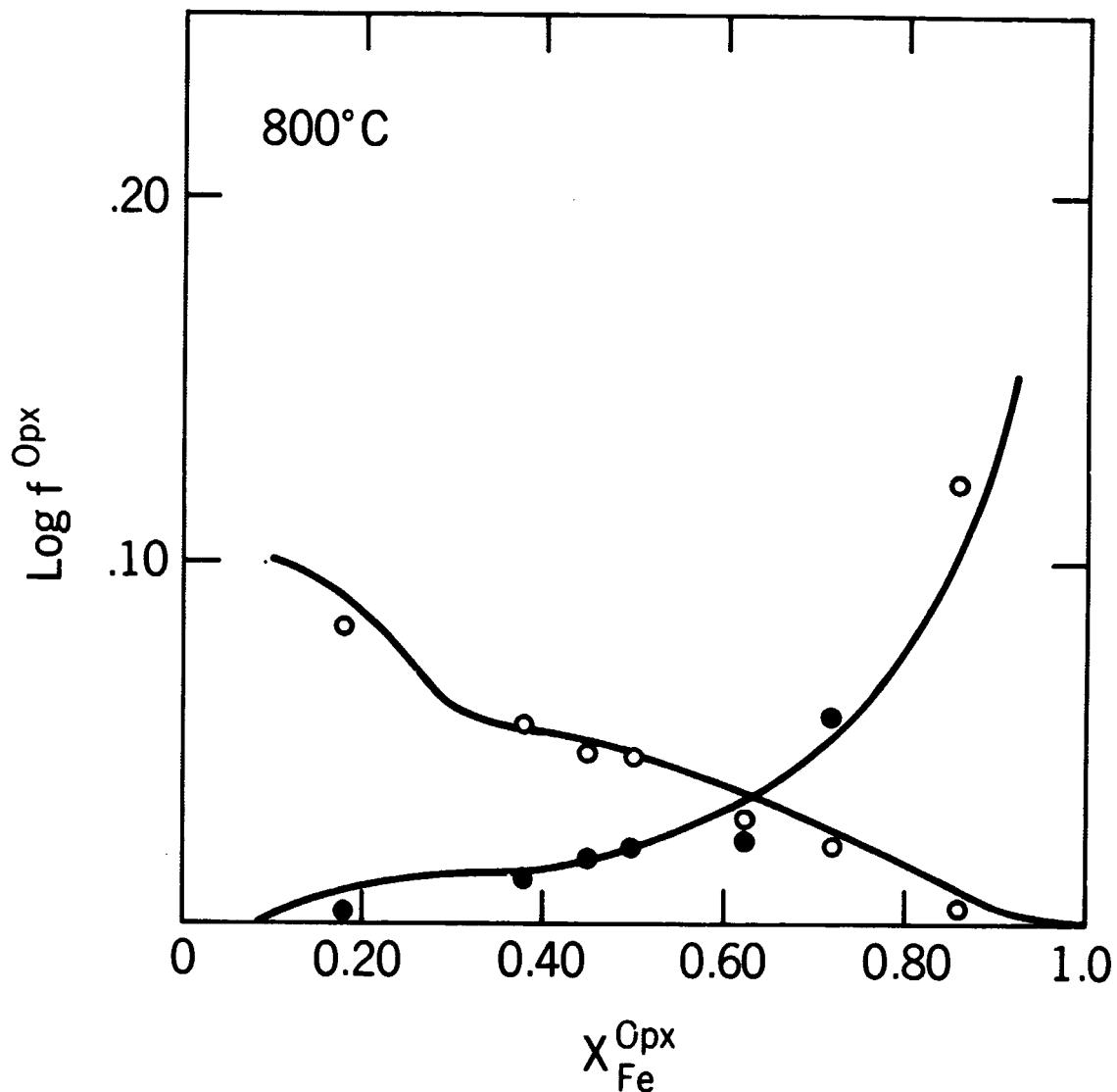


Figure 4d. Plot of log f against $X_{\text{Opx}}^{\text{Fe}}$ at 800°C.

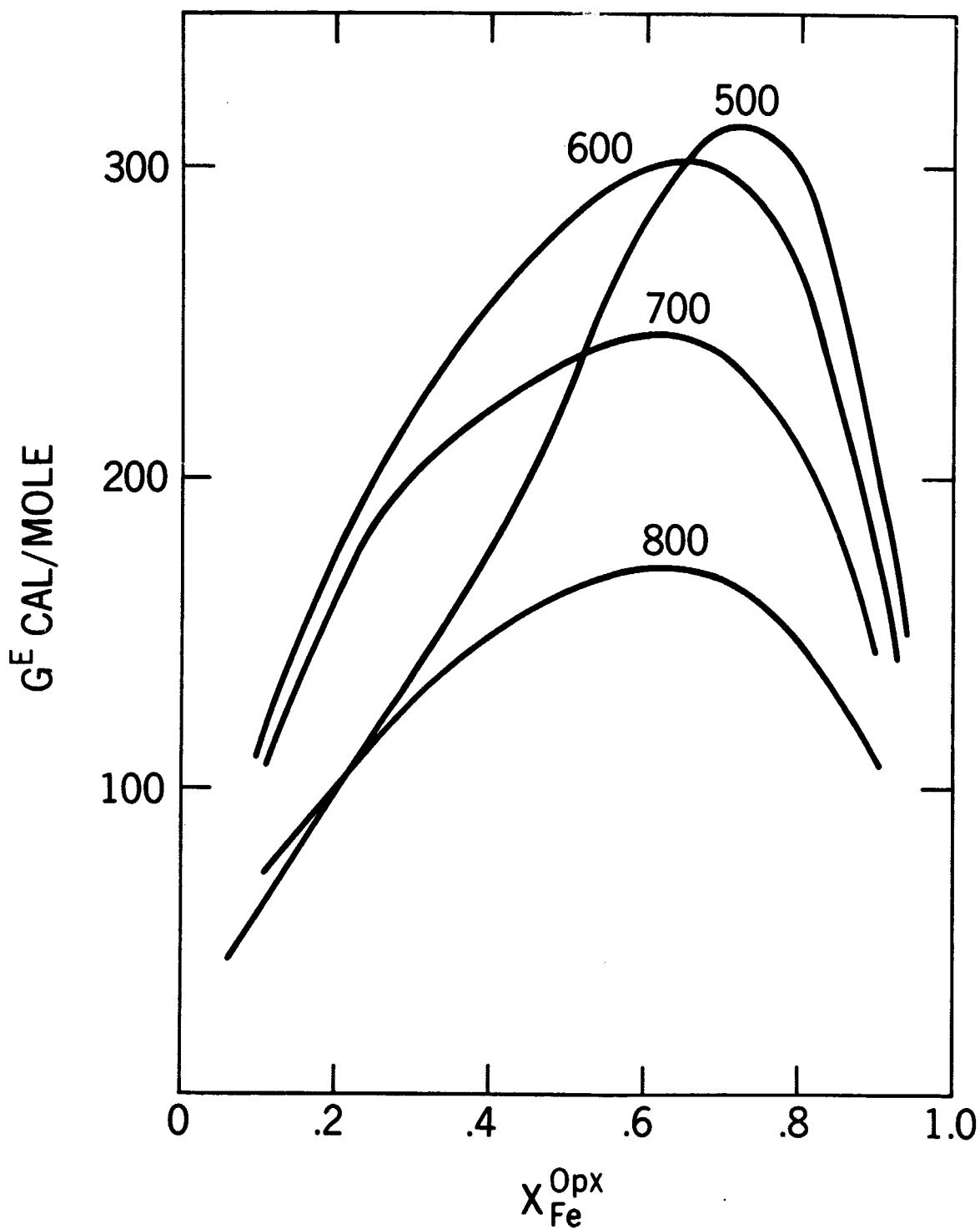


Figure 5. Plot of the excess free energy G^E obtained by using Guggenheim's (1937) expression with three constants A_0 , A_1 , and A_2 . These constants are calculated from the three constants B, C and D and are listed in Table 2.

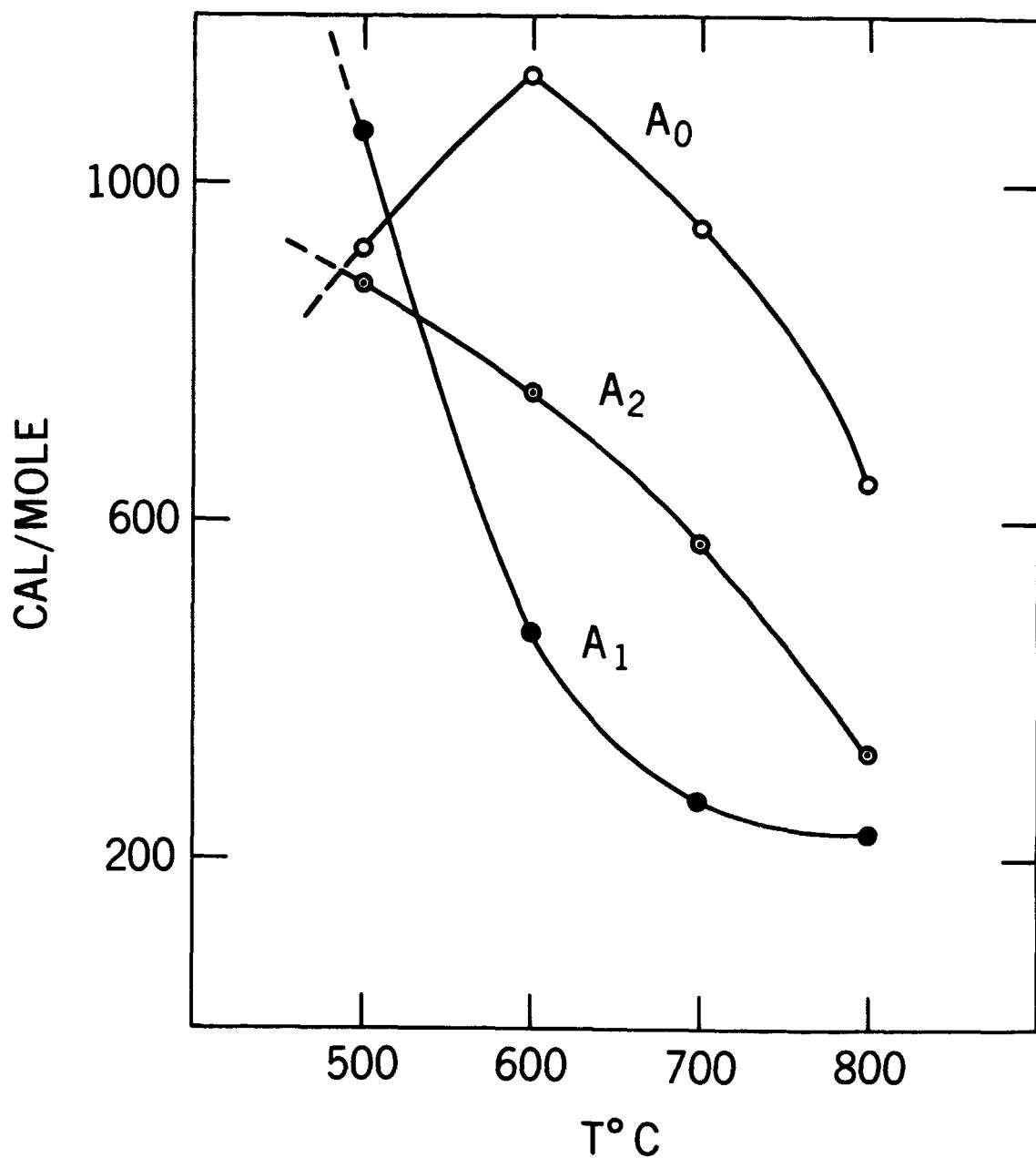


Figure 6. Plot of three constants A_0 , A_1 and A_2 in Guggenheim's (1937) expression for G_E , against temperature.

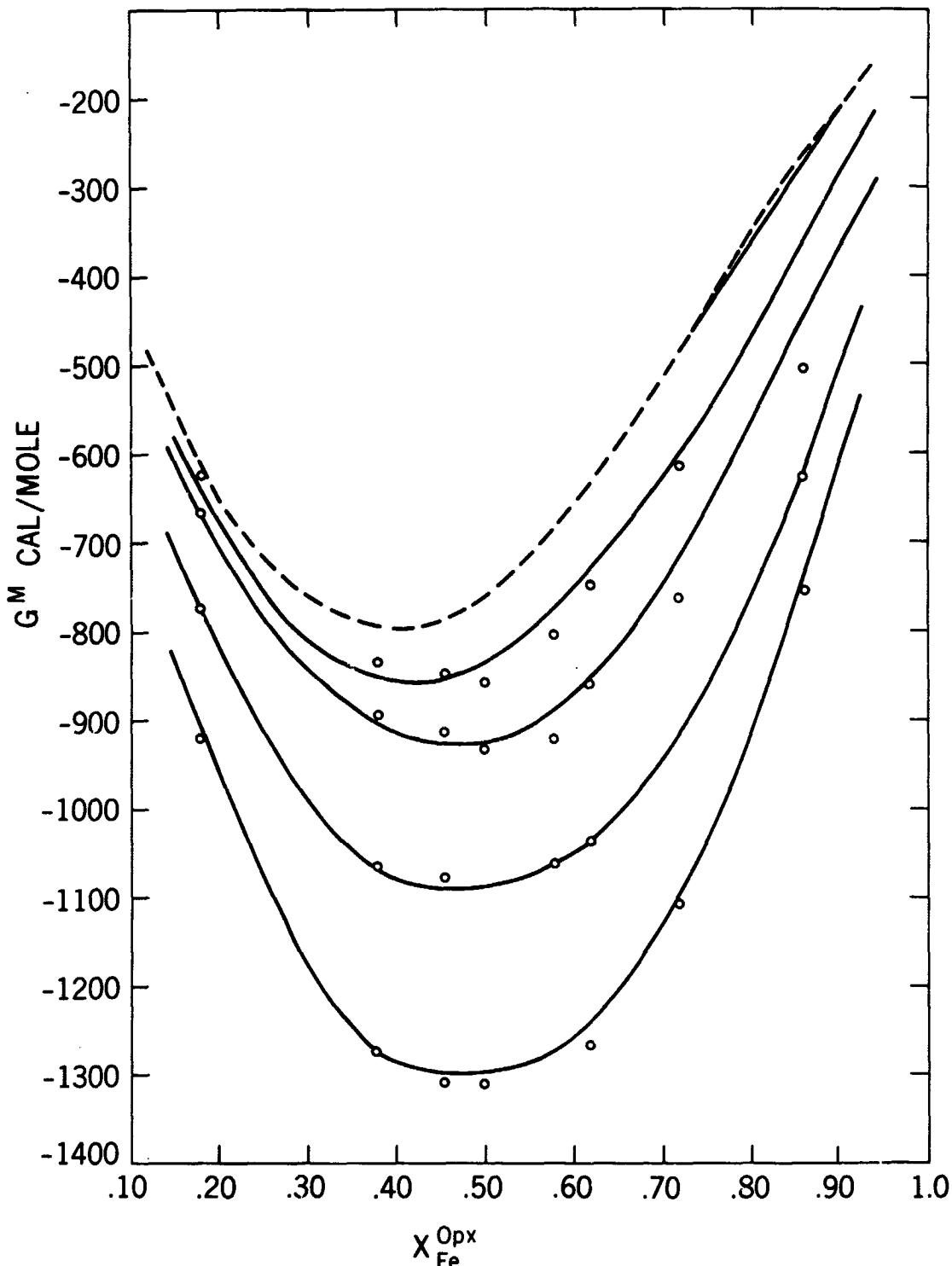


Figure 7. Plot of the free energy of mixing, G^M against X_{Fe} . The solid curves are drawn using Guggenheim's analytical expression for G^M . The open circles represent G^M for the samples calculated directly by using the equation: $G^M = X_{\text{Fe}} RT \ln \alpha_{\text{Fe}} + X_{\text{Mg}} RT \ln \alpha_{\text{Mg}}$. The dashed curve is based on extrapolated values of α_0 , α_1 , and α_2 to 400°C and shows that orthopyroxene with X_{Fe} between 0.75 to 0.90 would unmix into two co-existing pyroxenes.